

AD/A-006 299

EFFECTS OF ENVIRONMENT ON THE  
MECHANICAL BEHAVIOR OF METALS

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Prepared for:

Office of Naval Research

1974

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AD A 006299

077061

Final Report

EFFECTS OF ENVIRONMENT ON THE MECHANICAL  
BEHAVIOR OF METALS

Submitted to  
The Office of Naval Research  
Contract No. N00014-74-C-0279/NR036-087/11/06/73 (471)

Period: January 1, 1974 - December 31, 1974

by

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NATIONAL TECHNICAL  
INFORMATION SERVICE

MAR 4 1975

## EFFECTS OF ENVIRONMENT ON THE MECHANICAL BEHAVIOR OF METALS

### Summary

This investigation formed part of a broad program at Martin Marietta Laboratories directed toward understanding the surface- and environment-sensitive mechanical behavior of crystalline solids such as metals, metallic alloys, and ceramics as well as of noncrystalline, vitreous solids, for example, glass and fused silica. This program (a continuation of an earlier Contract, No. N00014-70-C-0255) was directed with the specific objective of providing an improved understanding of the mechanical behavior of metals in electrolytes, with the ultimate view of utilizing such understanding to increase the efficiency of operations such as metal cutting or forming and in the prevention of the environmental degradation of stressed materials, i. e., stress corrosion cracking, hydrogen embrittlement, etc. In each case, we believe that this study has been successful in meeting its objectives -- on the basis of some of the information generated in this fundamental research program, for example, a new metal cutting technique (electromechanical Machining, EMM) has been developed, patented, and is currently under pilot-scale study in the manufacturing facilities of Martin Marietta Corporation in Baltimore. Likewise, the mechanical behavior of metal electrodes has been examined from the point of view of the influence of variations in the surface charge density in the electrical double layer, and it has been found that both the flow and fracture characteristics of zinc electrodes is sensitive to such electrocapillary effects. In the case of hydrogen embrittlement, we have demonstrated that the intergranular embrittlement of nickel by cathodic hydrogen is associated with the accumulation of impurities -- particularly those that are effective hydrogen recombination poisons -- at the grain boundaries. The latter has particularly interesting implications when extended to other embrittlement phenomena (e. g., temper embrittlement) which are associated with segregated impurities. This Final Report summarizes the studies conducted under the sponsorship of the Office of Naval Research on the above topics.

## I. Introduction

It is a characteristic of a metal functioning as an electrode in an aqueous electrolyte, that a separation of charge or charge double layer develops at the metal/electrolyte interface. During the first two years of this program our principal effort was directed toward establishing and demonstrating the role of electrocapillary phenomena in crystal plasticity with, additionally, a secondary study of anisotropy in the polarization behavior of nickel monocrystal electrodes<sup>(1)</sup>. Our electrocapillary studies<sup>(2, 3)</sup> have shown that variations in the surface charge density (and, hence, surface energy and surface stress<sup>(4)</sup>) does affect the mobility of near-surface dislocations on the second-order pyramidal slip planes in zinc electrodes, provided that these dislocations produce surface steps. Recognizing that the suppression of glide by means of double layer phenomena should increase the tendency for brittle fracture, we turned our attention during the third and fourth years toward an evaluation of the possible role of the double layer in the embrittlement of metals. The latter began as a study of the embrittlement of polycrystalline nickel at cathodic potentials. However, in this case, it was found that the embrittlement which occurs<sup>(5-8)</sup> is a consequence of the interaction with hydrogen. Although double layer effects might contribute to some extent, other effects were so overwhelming that it was impossible to assess the significance of the double layer. Despite this, we regard our observations which associate the intergranular embrittlement of nickel with the accumulation of hydrogen recombination poisons at the grain boundaries as a major new finding, the implications of which may extend to other alloy systems which are known to be susceptible to hydrogen embrittlement. More recent studies of the fracture of zinc monocrystals as a function of electrode potential -- in which case there is no indication of damage by hydrogen -- have shown that fracture is in fact sensitive to electrode potential and it appears, to the surface charge distribution, i. e., the double layer.

This Final Report summarizes the studies carried out under the sponsorship of the Office of Naval Research on the above topics. Greater detail on the results of these studies may be obtained from the publications generated under the support of this contract. These publications are included as an appendix to this report.

## II. Summary of Research Conducted

### A. Polarization Anisotropy in the Passivation of Nickel Monocrystal Surfaces

Electrocapillary studies are meaningful only in the absence of surface films. Hence, as a preliminary to studies of the effects of electrode charge density on the dislocation mobility in nickel, the influence of crystal orientation on electrode kinetics was examined on the low index faces of nickel. In this work<sup>(1)</sup>, steady state potentiostatic polarization measurements on nickel surfaces indicated a strong anisotropy in passive current densities. It was found that this anisotropy is sensitive to such properties as the crystal growth axis, defect distribution on the surface examined, and the degree of epitaxy expected between the film and substrate. At passive potentials, for example, a {111} face cut from ingot grown parallel to the <110> behaved

markedly differently than an otherwise identical  $\{111\}$  face cut from an ingot grown parallel to the  $\langle 100 \rangle$  direction. A detailed analysis of this behavior emphasizes that one must not only characterize a monocrystal surface in terms of its intrinsic symmetry, but also in terms of its detailed structure, particularly the distribution and character of dislocations introduced during crystal growth which intersect such surfaces.

B. The Influence of Variations in Double Layer Charge Density on the Hardness of Metal Surfaces: Electrocapillary Effects

The most instructive of these studies were performed on low index surfaces of zinc monocrystals polarized to cathodic potentials in dilute aqueous electrolytes such as  $\text{Na}_2\text{SO}_4$ . These studies<sup>(2)</sup> have shown that the diamond pyramid hardness measured on the basal plane of zinc monocrystal electrodes passes through a maximum at about -1200 mV, S. C. E. This has been interpreted in terms of the effect of applied potentials (and, hence, the charge density) on the surface energy and surface stress<sup>(4)</sup> of the electrode -- i. e., electrocapillarity. Second-order pyramidal dislocations that intersect the basal planes leave surface steps in their trails as they glide about the indentation. If such steps exert a resisting force on the motion of pyramidal dislocations, then one expects that the extent of glide of such dislocations about the hardness impression would be a minimum (the hardness would be a maximum) when the work required to create these new surfaces is a maximum. This is precisely our observation. According to electrocapillary thermodynamics, the surface energy (better, the surface stress of a solid metal electrode<sup>(4)</sup>) passes through a maximum when the electrode surface is uncharged, i. e., at the potential of zero charge, pzc. The pzc is anisotropic, and, for the  $(11\bar{2}2)$  slip plane of zinc the pzc is believed to occur at -1200 mV corresponding to our measured hardness maximum.

As a check of this hypothesis, it was shown<sup>(2)</sup> that the mobility of edge dislocations about hardness impressions on the  $(10\bar{1}0)$  prism planes is insensitive to variations in electrode potential. In this case, edge dislocations on the pyramidal planes would have their Burgers vectors parallel to the  $(10\bar{1}0)$  free surface and would, therefore, not expose a surface step during slip about the indentation.

Likewise, if the above analysis is correct, the addition of surface active agents to the electrolyte should shift the pzc predictably, and the hardness maximum should be similarly displaced. Precisely that behavior has been observed<sup>(3)</sup> by adding specifically adsorbed ions ( $\text{Cl}^-$ ) in various concentrations to the  $\text{Na}_2\text{SO}_4$  electrolyte. Increasing the  $\text{Cl}^-$  concentration has the effect of decreasing the hardness and shifting the hardness maximum to more negative potential values, both of which are in accord with electrocapillary thermodynamics.

We have also demonstrated<sup>(3)</sup> that the same behavior experienced in diamond pyramid hardness measurements occurs in hardness testing with an oscillating pendulum. This is significant since the earliest reported correlations between surface charge and the mechanical behavior of metal electrodes refers to pendulum hardness measurements. However, there has been a long standing uncertainty as to whether the surface energy, friction or some other property of the solid is most responsible for the

pendulum hardness results. Our work<sup>(3)</sup> has shown that, as in the case of the diamond pyramid indentations on the basal plane, the slip which occurs about the depression left by the fulcrum of the oscillating pendulum occurs predominantly on the second-order pyramidal planes. Our view is that for metals the pendulum hardness technique principally measures the rate of energy absorption by slip processes in the near-surface region surrounding the indentation. Dislocation mobility (slip) is most resisted at the pzc because slip step "drag" is maximized as explained earlier. Thus, the rate of damping of the pendulum is expected to be a minimum (the pendulum hardness is a maximum) as observed<sup>(3)</sup>.

### C. Electrocapillary Effects in Fracture Phenomena

It is clear that variations in the work required to produce surface slip steps can affect the mobility of dislocations intersecting the free surface of a metal, and hence, can affect crystal plasticity. Recognizing as well the possibility that suppression of glide by means of double layer phenomena might increase the tendency toward brittle fracture, the emphasis during the third and fourth year of this program was oriented toward application of our understanding of electrocapillary phenomena to the environmental degradation and fracture of stressed metal electrodes. Our first attempt in this regard was to examine the potential-dependence of failure in polycrystalline nickel in the range of potentials where electrocapillary phenomena are likely to be most influential, i. e., near the pzc. This began as a study of the embrittlement of nickel at cathodic potentials. In a sense, nickel proved to be an inappropriate choice since we found that the embrittlement which occurred at cathodic potentials was undoubtedly associated with hydrogen. Even though double layer phenomena may contribute, hydrogen effects are so overwhelming that it is virtually impossible to assess the significance of the double layer. On the other hand, we regard our findings<sup>(5-8)</sup> in this study, which associated the intergranular embrittlement of nickel with the segregation of hydrogen recombination poisons to the grain boundaries, as a major new finding which may apply to other metals and alloy systems as well. The latter results are first summarized and then followed by a discussion of recent findings which permit evaluation of the contribution of electrocapillary phenomena to fracture -- namely, the potential dependence of cleavage fracture in oriented zinc monocrystal electrodes.

#### 1. The Intergranular Embrittlement of Nickel by Hydrogen: The Role of Grain Boundary Impurities

Nickel is a typically ductile metal. When nickel polycrystals are exposed under strain to cathodically produced hydrogen, however, they fail in an intergranular manner and with a surprisingly large loss of ductility<sup>(5)</sup>. The mechanism of embrittlement, which has been discussed elsewhere<sup>(5-7)</sup>, has been shown by means of Auger Electron Spectroscopy to be associated with the segregation of Sn and Sb, both of which are effective hydrogen recombination poisons, to the grain boundaries. In essence, we expect that the entry of hydrogen into the nickel specimens occurs preferentially in the proximity of the grain boundaries due to the presence therein of impurities which act to retard the combination of hydrogen atoms produced at

the cathode by the reduction of  $H^+$  from the electrolyte. The dependence of the fracture strain on applied potential<sup>(5-7)</sup> indicates that it is Sb which is the more critical segregated species and, moreover, that the gaseous hydride,  $SbH_3$ , is an even more efficient recombination poison. The latter is consistent with the view expressed many years ago by Smialowski.

The above association between impurities and microchemistry in hydrogen embrittlement may have applications as well to other systems that are known to be sensitive to hydrogen damage<sup>(8)</sup>. Alloys of iron are particularly interesting in this respect. For example, the temper embrittlement of steels has been associated with the segregation of impurities, many of which are, in fact, effective recombination poisons. It is also interesting that there is evidence to show that the tempering temperature range producing shortest time of steels exposed to hydrogen corresponds to the temper embrittlement range. It seems quite possible that the accumulation of poisons which occurs during tempering may lead to embrittlement in much the same way as described above for nickel. The same may be true of nickel-base alloys and other alloy systems.

## 2. Electrocapillary Effects in the Cleavage Fracture of Zinc Electrodes

In general, little attention is given to double layer phenomena in current thinking on the embrittlement of metal electrodes. Yet, the double layer is a fundamental characteristic of metals functioning as electrodes. Earlier work<sup>(2, 3)</sup> on this program has shown that variations in the electrode charge density can affect crystal plasticity. It is also a fact that an enormous field (about  $10^7$  V/cm) is present at the electrode surface due to the double layer. One, thus, anticipates that the cohesive strength of atomic bonds at the electrode surface may also be affected by changes in charge density. Hence, it seems likely that electrocapillary effects may induce embrittlement either by the suppression of glide (i. e., prevention of crack blunting, etc.) at crack tips or by the disruption of atom-atom bond strength.

In our recent work<sup>(9)</sup>, the potential dependence of fracture has been studied on zinc monocrystal tensile electrodes oriented such that the basal plane is perpendicular to the tensile axis. In this geometry, slip should occur predominantly on the second-order pyramidal planes, and it should be possible to correlate the fracture behavior with, for example, the known plastic response of pyramidal slip to electrode potentials<sup>(2, 3)</sup>. We have made some exciting observations: (a) in dead-load tests at 90% of the yield stress, we find that the time-to-failure is a sensitive function of the electrode potential and indeed passes through a sharp minimum at -1200 mV, S. C. E. -- i. e., at the pzc for the (11 $\bar{2}$ 2) slip planes; and (b) in constant strain rate tests, the fracture strain is a minimum at the pzc. It seems, therefore, that changes in electrode potential can affect not only the plastic behavior of metal electrodes but can also affect the initiation and propagation of cracks. This is a significant observation, not only with regard to the fracture of zinc, but also perhaps as well in terms of other examples of environmental embrittlement phenomena where the contribution of double layer effects had not been considered previously.

### III. Review Papers Prepared on Topics Related to This Contract

During the course of this program, three invited review papers have been written under the support of the Office of Naval Research. These are listed as references 10-12, copies of which are included in the appendix.

### IV. Conclusions

The specific objective of this program was to provide an improved understanding of the mechanical behavior of metals in electrolytes, particularly from the point of view of the influence of the charge double layer -- which is a characteristic of a metal functioning as an electrode -- on the plasticity and fracture of metals. We have found that the mobility of second-order pyramidal dislocations intersecting the free surface of zinc monocrystals is a sensitive function of the electrode potential provided that such dislocations produce surface steps which, in effect, act to resist their motion. Dislocation mobility was found to be a minimum (the hardness a maximum) at the pzc -- the point at which the work required to create new surfaces at slip steps passes through a maximum. Likewise, the cleavage fracture of zinc monocrystals was found to be potential-dependent and, in fact, the time-to-failure and fracture strain pass through distinct minima at the pzc. Hence, the double layer plays a role in both the flow and fracture of metal electrodes and may well contribute to other failure phenomena in which electrolytes are involved. In corollary experiments, the potential-dependence of the intergranular embrittlement of nickel was examined and found to be associated with the accumulation of hydrogen recombination poisons at the grain boundaries, and it has been suggested that similar phenomenology may apply to other metals and alloy systems that are susceptible to hydrogen embrittlement.



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